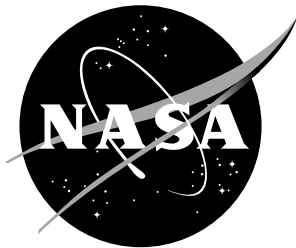# Radiation Induced Degradation of the White Thermal Control Paints Z–93 and Z–93P

D.L. Edwards, J.M. Zwiener, G.E. Wertz, J.A. Vaughn,
R.R. Kamenetzky, M.M. Finckenor, and M.J. Meshishnek

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October 1996

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TECHNICAL MEMORANDUM

RADIATION-INDUCED DEGRADATION OF THE WHITE THERMAL CONTROL PAINTS Z-93 AND Z-93P

INTRODUCTION

The Marshall Space Flight Center (MSFC) Space Environmental Effects Branch conducted a series of space environmental effects exposure tests to requalify a new potassium silicate binder used in the production of white thermal control paints Z-93 and YB-71. This requalification program was a joint effort between MSFC, the Aerospace Corporation, Lewis Research Center (LeRC), Wright Laboratories, and several other Government and industry facilities.

Z-93 was originally flight qualified with a potassium silicate binder (PS7) from Sylvania. Sylvania discontinued production of PS7 and a new vendor, PQ Corporation, was located to provide the potassium silicate binder.[1] The PQ Corporation denotes their binder as K2130.

The U.S. Air Force sponsored the Aerospace Corporation to lead this program to requalify three paints, Z-93, YB-71, and S13G/LO-1. The paints using the potassium silicate binder PS7 are denoted as Z-93 and YB-71, while the paints using the K2130 binder are denoted as Z-93P and YB-71P. The S13G/LO-1 paint utilizes a room-temperature vulcanized (RTV) binder, and testing on this paint was not performed at MSFC.

The Air Force initially designated this requalification program as a 1-year effort. In reality, the program lasted 3 years. MSFC's involvement in this requalification effort was requested, by the Aerospace Corporation, midway into the 3-year program. The task that the MSFC Space Environmental Effects Branch agreed to perform was a comparison analysis of the two aforementioned paints utilizing the original (PS7) and new (K2130) binders. Two samples per test would be simultaneously exposed to combined space environmental effects (CEE). One of these samples would have the PS7 binder and the other would have the K2130 binder. This report details the comparison analysis of Z-93 and Z-93P when simultaneously exposed to CEE.

EXPERIMENTAL PROCEDURE

Description of the Facility

The Space Environmental Effects Branch at MSFC operates the CEE test system. This system provides the unique capability to irradiate material to a simultaneous or sequential exposure to a simulated space environment and perform in-vacuo reflectance measurements. The simulated space environment consists of protons, low-energy electrons, high-energy electrons, vacuum ultraviolet (VUV), and near ultraviolet (NUV) radiation. The CEE test system is shown in figure 1. This test system is composed of all Conflat[TM] metal seals and is maintained at a base pressure of 5×10^{-8} torr with four ion pumps. High-energy electrons and protons propagate through the vacuum from the accelerators to the test chamber through two separate beam lines. Each beam line is equipped with a beam profile monitor (BPM) and Faraday cups. The BPM is a device that measures the intensity distribution and position of a charged particle beam.[2] The Faraday cup measures the charged particle beam current. Each beam line has a Faraday cup that is remotely moved into and out of the charged particle beam path.

These Faraday cups are identified as the in-line Faraday cups. The test chamber has a Faraday cup array that will be described later. The CEE test chamber is a six-way cross with 13.25-in diameter
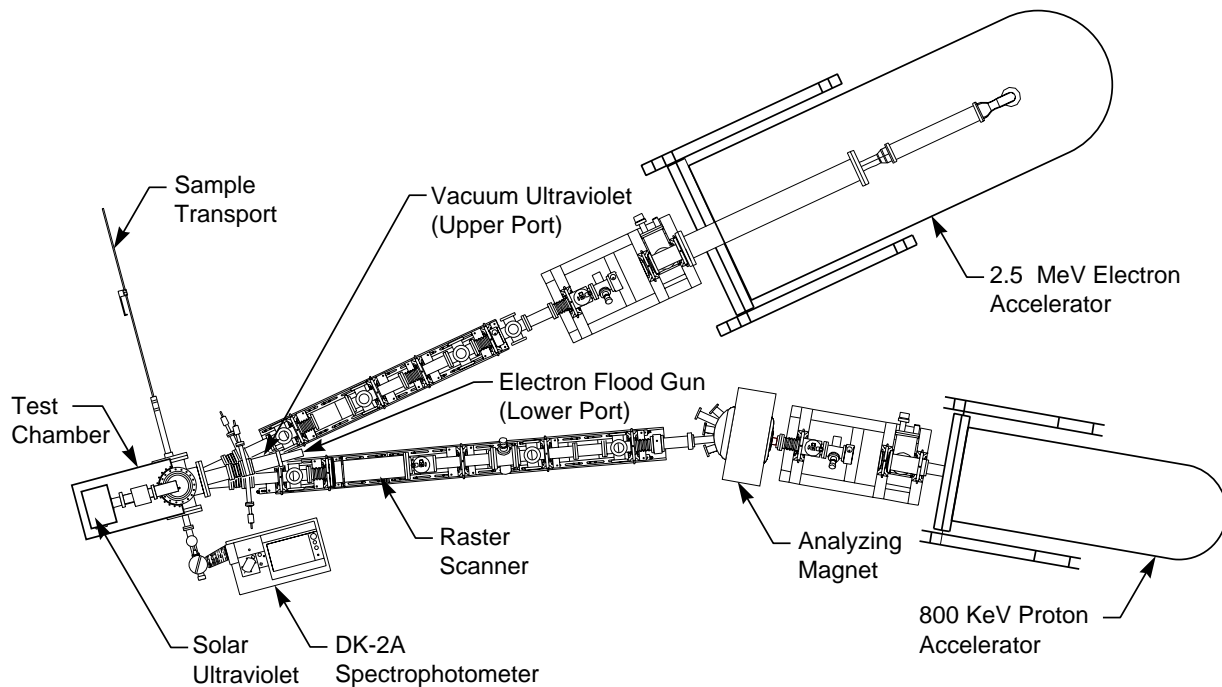
Figure 1. CEE test system.

Conflat™ flanges on all six ports. All space environmental sources are focused on the center of the test chamber. The sample exposure position is the center of the test chamber. Below the sample exposure position is the array of Faraday cups. Each Faraday cup is oriented to collect charge from a specific charged particle source. Figure 2 shows the Faraday cup array as mounted in the CEE test chamber. A temperature-controlled sample holder transports the two 1-in diameter samples in the horizontal plane from the sample exposure position to the integrating sphere for in-vacuo reflectance measurement. The sample holder was maintained at 21 ˚C for this Z-93/Z-93P comparison test to reduce any sample heating effects.

During a CEE exposure, the samples are rotated so that the sample normal is +45˚ off the horizontal plane. This orientation allows the samples to be simultaneously exposed to all sources. The high-energy electrons and protons impinge the sample surface at a 45˚ angle of incidence.

The NUV irradiation also impinges at a 45˚ angle to the sample surface. The VUV and low-energy electrons impinge the sample at angles of 35˚ and 55˚, respectively. The individual space environmental sources are described in the following paragraphs.

High-Energy Electrons

The high-energy electrons originate from a National Electrostatics Corporation (NEC) Pelletron particle accelerator. The energy range of the electrons is selectable from 200 KeV to 2.5 MeV. Electron flux is also selectable from a minimum value of 1 nA/cm^2 to a maximum of 50 µA/ cm^2 at the high-energy limit. The electron flux is monitored by two Faraday cups. The in-line Faraday cup is located midway between the accelerator and the test chamber, and the other Faraday cup is part of the Faraday cup array and is located in the test chamber 1.3 cm below the sample exposure position. The in-line Faraday cup is remotely moved out of the high-energy electron beam path during exposures. The Faraday cup located in the test chamber monitors the electron beam flux in situ. The electron beam is dispersed by means of an aluminum scattering foil. The scattering foil is 0.025 mm thick and is located a distance of 35.5 cm from the sample position.
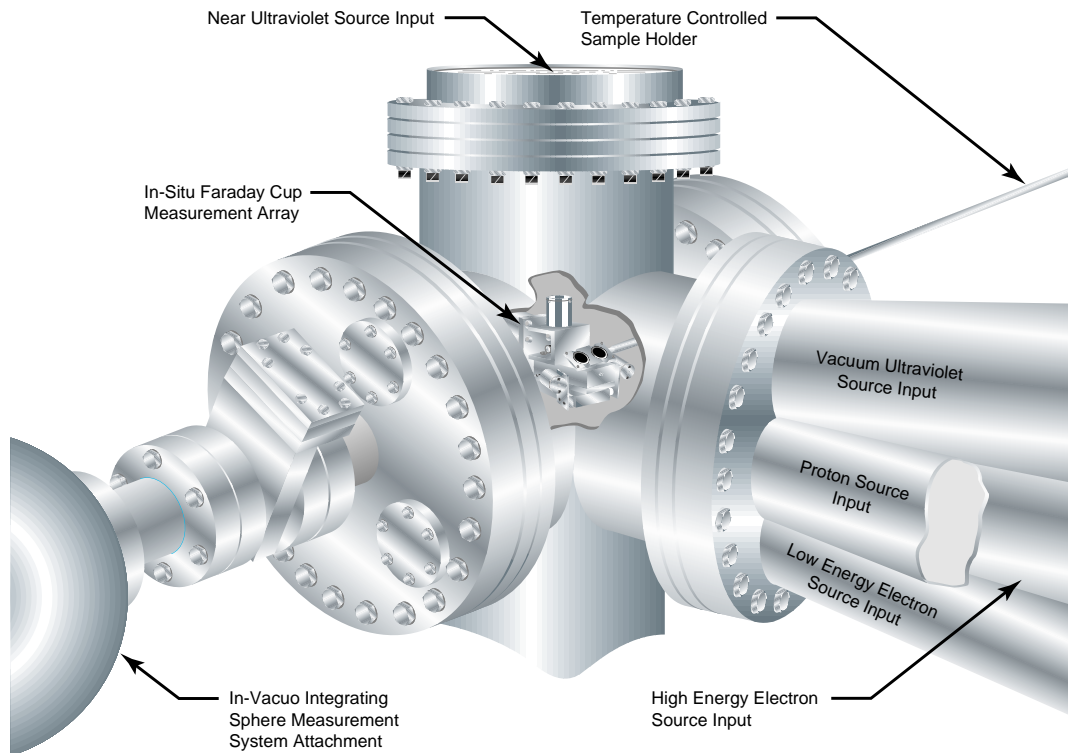
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Figure 2. Combined environmental test chamber.

Protons

The protons originate from a second NEC Pelletron accelerator. The energy range of the protons is selectable from 50 to 800 KeV. Proton flux is also selectable from a minimum value of 1 nA/cm^2 to a maximum of 50 μA/cm^2 at the high-energy limit. The proton beam line incorporates an analyzing magnet that mass analyzes the proton beam and thus provides a mono-energetic proton beam for sample exposure. The proton beam flux is monitored by two Faraday cups. The in-line Faraday cup is located midway between the analyzing magnet and the test chamber, and the other Faraday cup is part of the Faraday cup array and is located in the test chamber 1.3 cm below and 3.8 cm to the right side of the sample position. The in-line Faraday cup is remotely moved out of the beam path during sample exposures. The Faraday cup in the test chamber monitors the proton beam flux in situ. The proton beam is dispersed using a raster scanner that scans the beam over a tunable coverage area. Characterization tests, which correspond with the manufacturer's specifications, indicate that the raster scanner provides less than 2 percent variation of charge across the sample surface.[3]

Low-Energy Electrons

The low-energy electrons originate from a Kimball Physics electron flood gun. The energy range of the electrons is selectable from 1 to 50 KeV. Electron flux is also selectable from a maximum value of 1 nA/cm^2 at the lower energy limit to 500 nA/cm^2 at the higher energy limit. The electron flux is measured by using a Faraday cup located in the Faraday cup array positioned in the test chamber 1.3 cm below and 3.8 cm to the left side of the sample exposure position. Dispersion of the electron beam is accomplished within the flood gun firing unit, and characterization tests indicate less than 2 percent variation of charge across the sample surface. The electron flood gun firing unit is located 61 cm from the sample exposure position.

Solar Ultraviolet (Near Ultraviolet)

The NUV source (mercury xenon) is located external to the vacuum test chamber and irradiates through a fused silica view port located on the top port of the CEE test chamber. A water filter successfully attenuates the bulk of the infrared portion of the spectrum, and a 90° front surface mirror reflects the NUV into the test chamber. A fluorescent-coated diode is permanently mounted in the test chamber 2.5 cm behind the sample position and constantly monitors the NUV intensity. Pretest characterization of the NUV source using a spectral radiometer provided calibration data to determine the relationship between NUV intensity and diode current.

Vacuum Ultraviolet

The VUV source (deuterium) is located in the vacuum chamber and positioned at a distance of 102 cm from the sample position. A fluorescent-coated diode, mounted on a rotary motion feedthrough in the CEE test chamber, measures the VUV intensity. The diode can be manually rotated to a position 2.5 cm in front of the sample position and normal to the VUV beam to obtain an intensity measurement. Once the measurement is recorded, the diode is rotated out of the beam path for continued VUV exposure. Pretest characterization of the diode provided the relationship between VUV intensity and diode current.

Supporting Systems

The CEE test chamber is equipped with a Faraday cup array containing three Faraday cups. These Faraday cups were described briefly in the previous paragraphs and are shown mounted in the CEE test chamber in figure 2. Each cup is oriented to measure a separate charged particle source. The cups are not biased but have an aspect ratio of at least 5 to 1. This aspect ratio allows for adequate collection of secondary electrons and provides accurate beam current measurement.

Figure 3 shows the exposure geometry within the CEE test chamber. The side-view drawings in figure 3 show the VUV and low-energy electron interaction angles α and β, respectively. In the CEE test system, α and β are 10°. The side-view drawing also shows the NUV interaction angle γ, which is 4°. The top-view drawing shows the angles of sample surface incidence of the protons and high-energy electrons to be δ and ϕ. In the CEE test system, δ and ϕ are 10°.

This test system offers the unique capability of in-vacuo reflectance measurement using an Edwards-type integrating sphere, Beckman DK2A spectrophotometer with a Gier-Dunkle attachment to perform total hemispherical spectral reflectance measurements.

CONTAMINATION

A previous test, which subjected a trial Z-93 sample to a low dose of CEE, indicated the presence of a surface contaminant. This Z-93 sample was prepared by AZ Technology. Figure 4 shows the detrimental effects of a photodeposited surface contaminant on Z-93. This Z-93 sample was exposed to a low dose of CEE's detailed in table 1. After the exposure, an in-vacuo reflectance spectrum of the Z-93 sample was obtained. The CEE test chamber was repressurized with air to ambient pressure prior to the acquisition of the in-air reflectance spectra also shown in figure 4.

The Z-93 sample was placed in a standard sample holder and kept on a shelf in the laboratory. A reflectance spectrum was taken after 5,160 hours of ambient exposure. The data shown in figure 4 indicate that the reflectance of this specific contaminant will not immediately recover when exposed to air, but low levels of surface contaminate will slowly recover reflectance with prolonged ambient exposure.

Side View

Side View

Vacuum Ultraviolet

Horizontal Plane

α

β

Low Energy Electrons

Top View

Top View

δ

φ

Protons

0°

High
Energy
Electrons

Near Ultraviolet

Normal

γ

VUV

α

Horizontal Plane
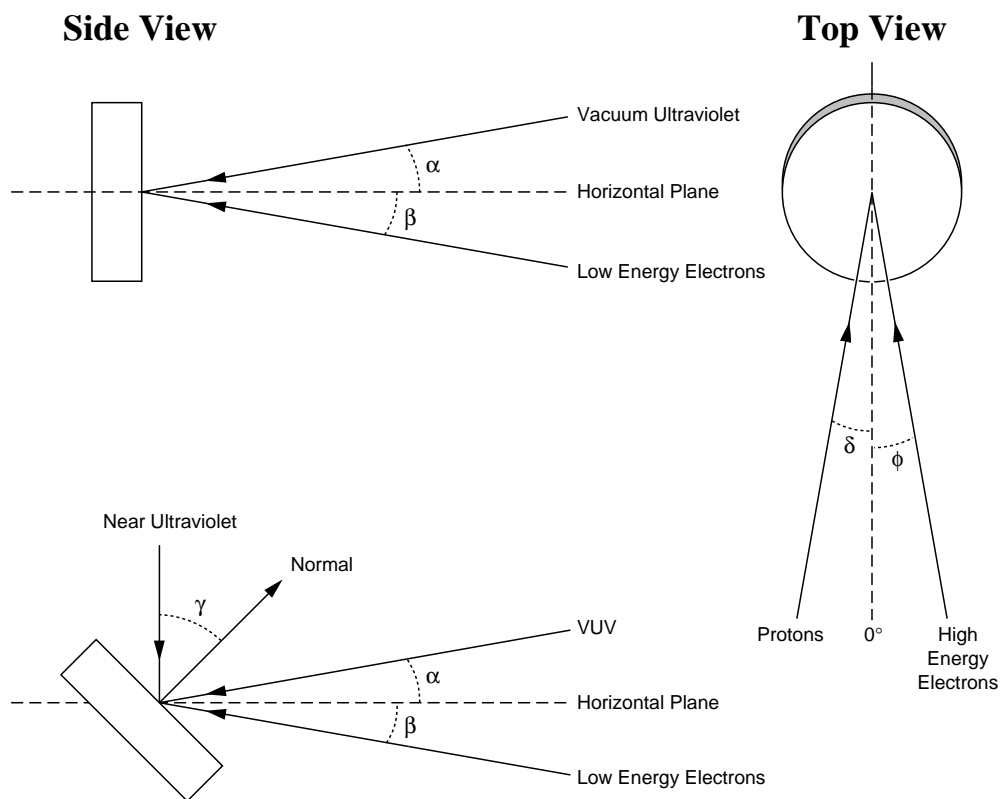
β

Low Energy Electrons

Figure 3. Sample exposure geometry in the CEE test chamber.
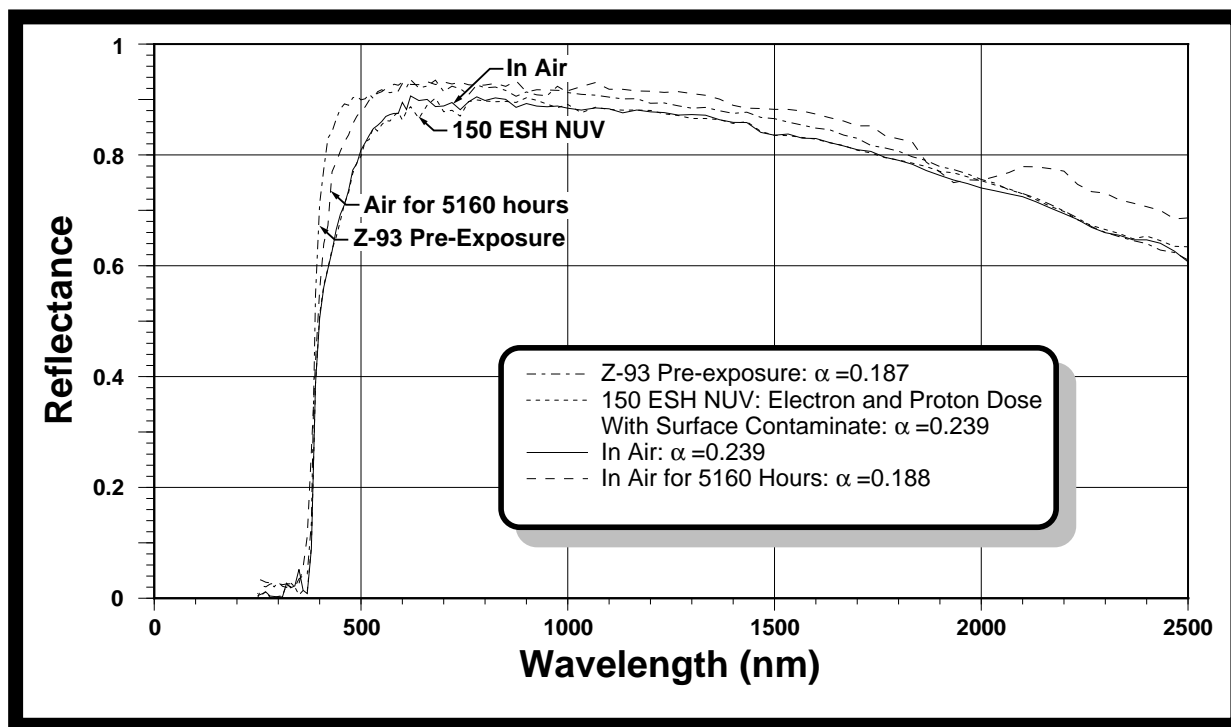

Figure 4. Reflectance spectra showing photodeposited surface contaminant on Z-93 accumulated during a low dose CEE exposure.

Table 1. Dose applied to the Z-93 sample shown in figure 4.

Source	Fluence
NUV	150 ESH at 2 UV Suns
VUV	150 ESH at 2 UV Suns
700 KeV protons	5×10^{13} protons/cm^2
200 KeV protons	6.3×10^{13} protons/cm^2
100 KeV protons	6.2×10^{13} protons/cm^2
200 KeV electrons	1.1×10^{14} electrons/cm^2
50 KeV electrons	1.9×10^{14} electrons/cm^2

Supporting indicators, which showed that a contaminant was present, were rapid loss of VUV intensity and rapid reduction of electron flux from the electron flood gun. A visible contaminant layer was observed accumulating on the VUV source window; however, this layer was removed with solvent cleaning. The VUV intensity was reestablished after the contaminant layer was removed. The reduction of electron flux, from the electron flood gun, was not recoverable. The initial electron flux could not be restored even after extensive cleaning of the electron flood gun firing unit. The initial electron flux was eventually restored by removing the contaminated firing unit and installing a new electron flood gun firing unit. The contaminated electron flood gun firing unit was sent to the factory for refurbishment.

A procedure for decontaminating the CEE test system was developed by the Space Environmental Effects Branch. The first step was to identify and remove all possible contamination sources from the CEE test system. One source of contamination was located internal to the VUV source. The Hamamatsu™ VUV source has an O-ring inside the source. This O-ring was coated, at the factory, with a thin layer of lubricant. Solvents were used to remove this thin layer of lubricant from the O-ring. All other internal VUV surfaces were cleaned using solvents. Once all contamination sources were removed, the CEE test system was partially disassembled and cleaned using conventional solvents. All small components were subjected to a vacuum bakeout for 48 hours in a vacuum of 5×10^{-8} torr. The temperature during the vacuum bakeout was 150 ˚C. The CEE test system was reassembled after the vacuum bakeout.

A bakeout of the entire CEE test system for 1 week at 100 ˚C was performed after reassembly. The pressure in the CEE system was 2×10^{-7} torr and was reduced to 5×10^{-8} torr after 1 week. In order to determine when the CEE system was clean, a residual gas analyzer (RGA) was installed. The system was monitored until all molecular gases above 44 AMU (below which represent the atmospheric constituents) were undetectable. All peaks above 44 AMU can be considered as system contaminants. At this point, the system was repressurized and clean, characterized optical witness samples (OWS) were installed.

The system was pumped down and the OWS mirrors were irradiated with the NUV source for 24 hours. After repressurization, the OWS mirrors were measured to determine if the VUV reflectance values changed. To our surprise, the OWS mirrors were degraded, which meant that the system was still contaminated. In order to achieve a higher level of cleaning, an oxygen glow discharge system was assembled in the CEE test system. Oxygen glow discharge was maintained for 2 weeks. After the 2 weeks of glow discharge, the CEE test system was ready for final contamination-free verification.

The CEE test system was verified to be contamination-free utilizing a technique developed within the Space Environmental Effects Branch. The contamination-free verification test is based on the principle

of photodeposition of contaminants on surfaces. This technique requires that OWS be exposed to NUV to induce photodeposition of contaminants. The OWS used in the contamination-free verification test were chosen to be Z-93 and an aluminum alloy (2219). Originally an OWS mirror and an aluminum alloy (2219) were utilized to monitor contamination in the CEE test system. The OWS mirrors that were used to monitor contamination consist of a first surface mirror with a MgF_2 layer over aluminum on a fused silica substrate. The specular reflectance of the OWS mirror is measured in a VUV reflectometer between 121.6 and 200 nm, to determine if degradation from contamination is present. The OWS mirror was replaced with the Z-93 OWS due to the applicability to the CEE test system, which measures total integrated reflectance above 250 nm. The OWS mirrors are applicable for detecting specular reflectance effects below 200 nm. The Al alloy 2219 was utilized due to past experience indicating optical stability in a low dose radiation environment.[4]

The criteria for the aluminum alloy 2219 OWS for contamination-free verification was less than ±3% ΔR/R change in the reflectance spectra. The criteria for the Z-93 OWS was less than ±3% ΔR/R change in the reflectance spectra above the fundamental absorption edge. These criteria were applied to both samples after a NUV exposure of 200 ESH in a vacuum of 5×10^{-8} torr. It was theorized that photo-induced deposition of contaminates will not be selective for these surfaces. It was further theorized that any photodeposition of contaminates would be detectable on the Z-93 and 2219 samples. Both samples were exposed to NUV for 100 hours at 2 Suns intensity. After the 200 ESH exposure, both samples were analyzed using the in-vacuo reflectance technique. The Z-93 reflectance spectra indicated slight degradation; however the aluminum 2219 spectra showed no change. The OWS's were subsequently exposed to an extreme dose of NUV and 50 KeV electrons over a 4-week period. In-vacuo reflectance measurements were made twice a week, with the results continuously showing increased degradation of the Z-93 and no change, exceeding the contamination-free criteria, of the aluminum alloy 2219.

This test was terminated after an exposure of 1,156.5 ESH NUV and 50 KeV electrons at a fluence of 3.53×10^{15} electrons/cm^2 and the CEE test chamber was repressurized to atmospheric pressure using air as a fill gas. The results of this test are shown in figure 5. Table 2 describes the dose applied to the Z-93 and 2219 witness samples shown in figure 5.
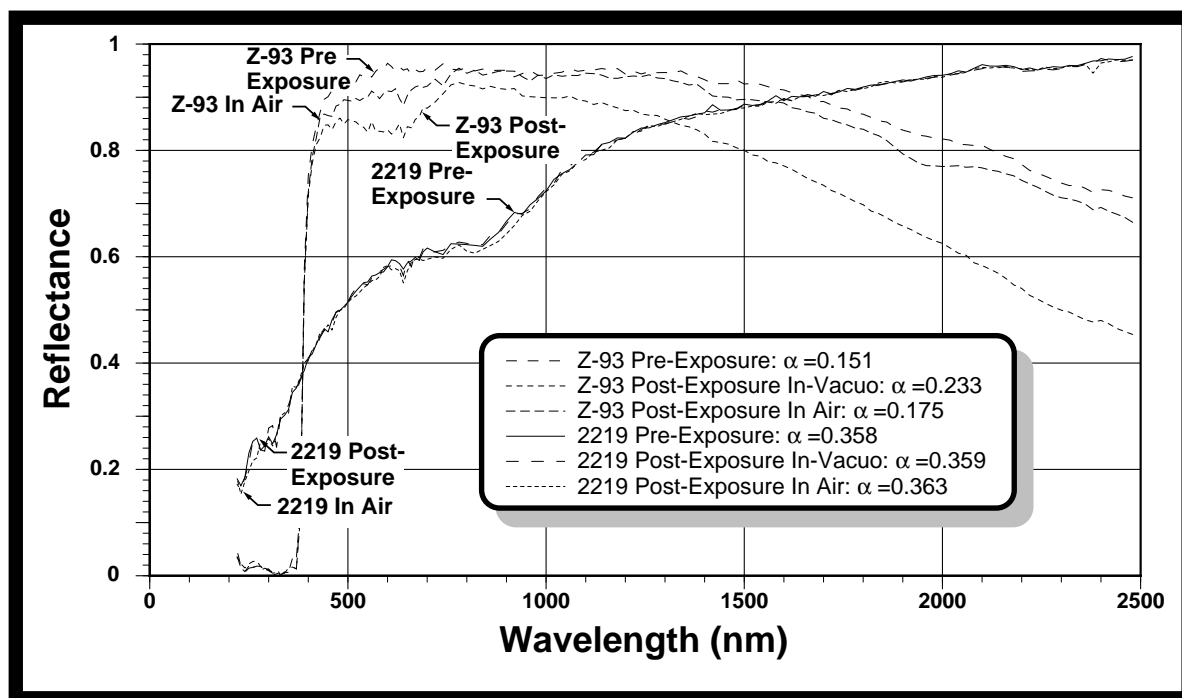

Figure 5. In-vacuo reflectance spectra of Z-93 and Al alloy 2219 exposed to CEE and repressurized with air.

Table 2. Dose applied to the Z-93 and Al alloy 2219 shown in figure 5.

Source	Fluence
NUV	1,156.5 ESH at 2 UV Suns
50 KeV electrons	3.53×10^{15} electrons/cm^2

Conclusions of this test are two-fold: (1) the Z-93 sample showed optical degradation after the exposure described in table 2 and the 2219 sample showed no change in reflectance, and (2) the Z-93 showed substantial reflectance recovery when repressurized with air. The degradation in the Z-93 was believed to be induced by NUV and electron irradiation, not contamination. If the degradation was attributed to contamination, it is believed that the Al 2219 would have an absorption peak appear in the spectra and the Z-93 would not show rapid substantial reflectance recovery when repressurized with air.

EXPOSURE SEQUENCE

Two white thermal control paint samples were obtained from the Illinois Institute of Research and Technology Institute (IIRTI): a Z-93 sample, number A-042 of batch R155 with the PS7 binder, and a Z-93P sample, number X-11 of batch S044 with the K2130 binder. These samples were placed in the CEE test chamber and a pre-exposure in-vacuo reflectance measurement was taken when the vacuum level in the chamber reached 8×10^{-7} torr.

The NUV and VUV exposures were initiated, after the pre-exposure measurement was obtained, with both sources providing nominally 2 UV Suns intensity on the samples. The VUV intensity of 2 UV Suns was measured over the wavelength range from 120 to 200 nm. The samples were then exposed to 700 KeV protons; however, due to a faulty Faraday cup in the test chamber, the proton exposure was quickly terminated. Several attempts to correct the problem failed and resulted in several short but intense proton exposures being applied to the Z-93 and Z-93P samples.

A visual inspection during this proton exposure indicated fluorescence emanating from the Z-93 sample; however, no fluorescence was observed from the Z-93P sample. The proton dose the samples received was short but unknown; however, due to the fluorescence observed, it was ascertained that the Z-93 sample received a larger dose than the Z-93P. Approximately 30 minutes after the unknown proton exposure, in-vacuo reflectance measurements were obtained on the two samples. These data are shown in figure 6. Figure 6 shows a substantially larger decrease in reflection for the Z-93 sample after the proton exposure. Sample exposure to electrons continued for approximately 3 weeks, with in-vacuo reflectance measurements made on a weekly basis. The samples were continuously exposed to NUV and VUV throughout the duration of this test, and the intensities were maintained at nominally 2 UV Suns. Sample exposure to 50 and 200 KeV electrons varied in duration from day to day; however, the beam current for each source was maintained at 1 nA/cm^2 during each electron exposure.

The first week of testing consisted of exposing both samples to 50 KeV electrons for a total of 9 hours with simultaneous NUV and VUV exposures. This 50 KeV electron exposure was distributed over 2 days, with 4.5 hours of exposure per day. Figure 7 shows the status of the samples after the first full week of testing. The total dose to the samples, prior to the reflectance measurement shown in figure 7, was 478.5 ESH of NUV and VUV, 50 KeV electrons at a fluence of 3.79×10^{14} electrons/cm^2, and the unknown proton exposure. Notice the partial recovery in reflectance of the Z-93 sample over the wavelengths 800 nm to 2,500 nm. This recovery phenomena has been documented in other literature.[5] A roughly formulated theory is presented in the conclusion section in an attempt to explain this partial
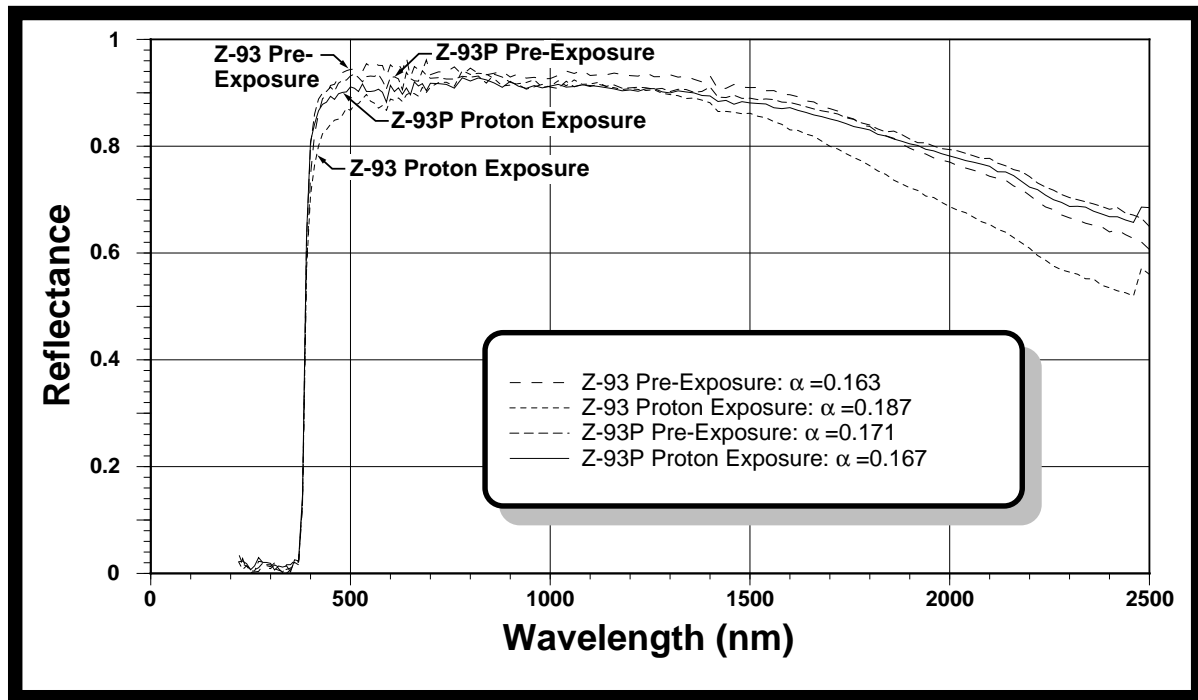
Figure 6. In-vacuo reflectance spectra of Z-93 and Z-93P after the undefined proton exposure.

recovery. Figure 7 also clearly shows the increased degradation due to the first full week's exposure. Comparison of the two samples indicates that the reflectance spectra of Z-93 and Z-93P are degrading similarly.
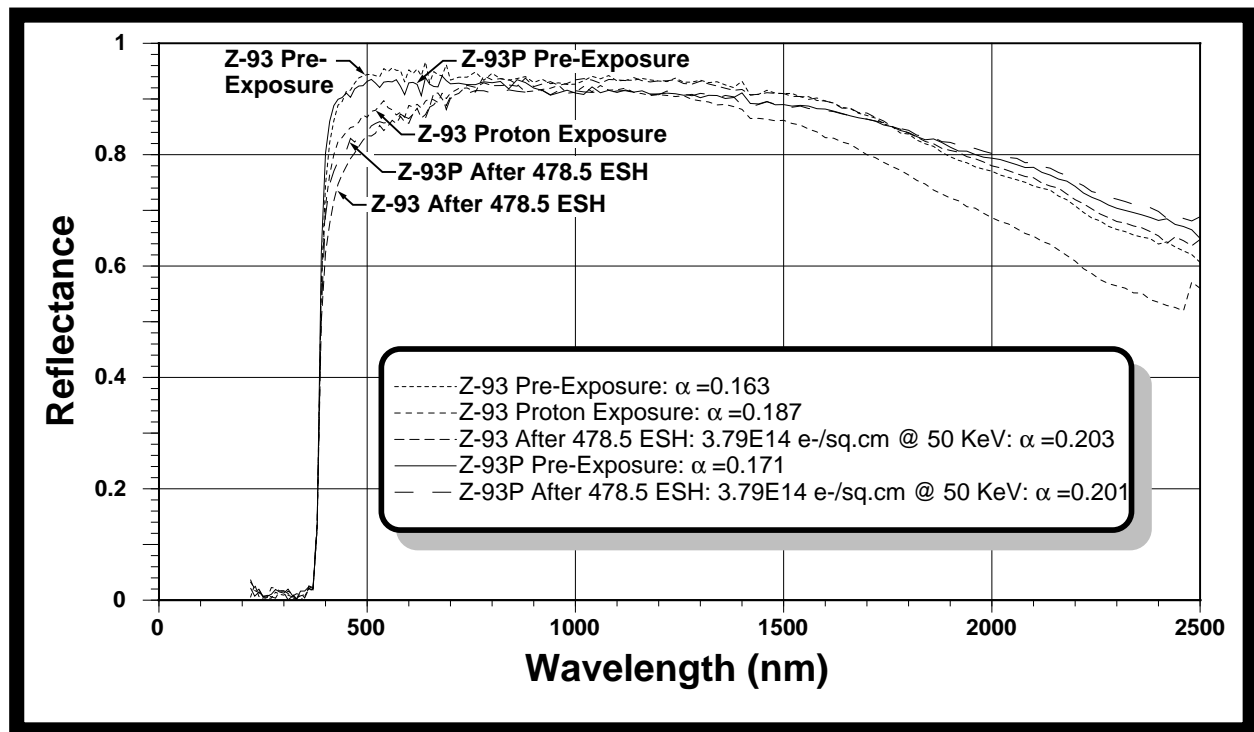

Figure 7. In-vacuo reflectance spectra of Z-93 and Z-93P showing reflectance degradation after exposure to 478.5 ESH of NUV and VUV, 50-KeV electrons at a fluence of 3.79×10^{14} electrons/cm^2.

The next measurement was obtained after the second week of sample exposure. During this second week, the samples were exposed to NUV, VUV, 50-KeV electrons, and 200 KeV electrons.

The duration of 200-KeV electron exposure during this second week was 3.5 hours distributed over 2 days. The 50-KeV electron exposure during this second week was 7 hours distributed over 3 days. The 200- and 50-KeV electron exposures were performed simultaneously with the NUV and VUV exposures. Figure 8 shows the Z-93 and Z-93P reflectance after the second week of testing. The total dose the samples received, prior to the reflectance measurement shown in figure 8, was 684.5 ESH of NUV and VUV, 50-KeV electrons at a fluence of 7.35×10^{14} electrons/cm^2, 200-KeV electrons at a fluence of 1.33×10^{14} electrons/cm^2, and the unknown proton exposure. Figure 8 shows further degradation of the reflectance spectra of both samples after the second week's exposure. Both samples are shown to have similar degradation spectra at this stage in the test.

The CEE exposure portion of the test was terminated after the third week, with a total dose of 953.5 ESH of NUV and VUV, 50 KeV electrons at fluence of 1.2×10^{15} electrons/cm^2, 200-KeV electrons at a fluence of 7.35×10^{14} electrons/cm^2, and the unknown proton exposure. During this third week, the 200-KeV electron exposure was slightly over 14.5 hours and the 50 KeV electron exposure lasted 7 hours.
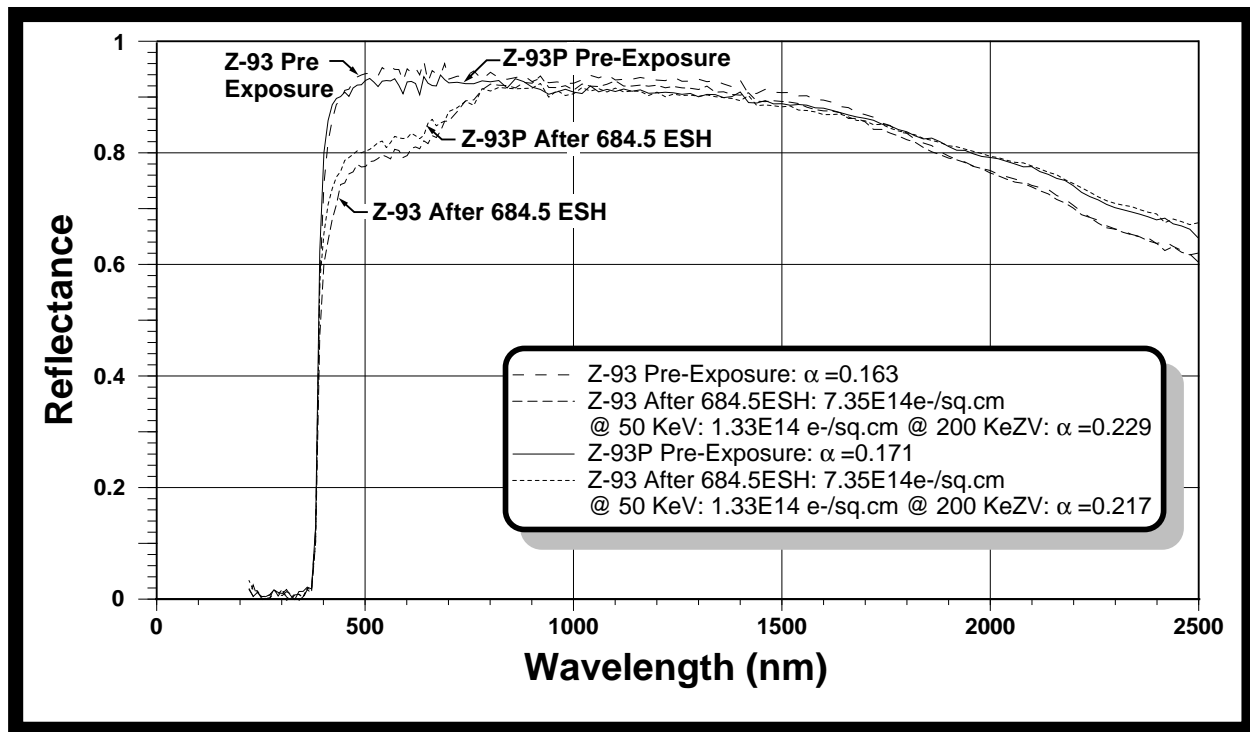

Figure 8. In-vacuo reflectance spectra of Z-93 and Z-93P after exposure to 684.5 ESH of NUV and VUV, 50-KeV electrons at a fluence of 7.35×10^{14} electrons/cm^2 and 200-KeV electrons at a fluence of 1.33×10^{14} electrons/cm^2.

The 200-KeV electron exposure was accomplished over 3 days, and the 50-KeV electron exposure was distributed over 2 days. The sample was exposed to NUV, VUV, and 200 KeV electrons on the last day of the exposure test. The reflectance spectra of Z-93 and Z-93P after this total, or terminating, dose is shown in figure 9. This figure shows that both samples degraded similarly at the terminating dose of this test.
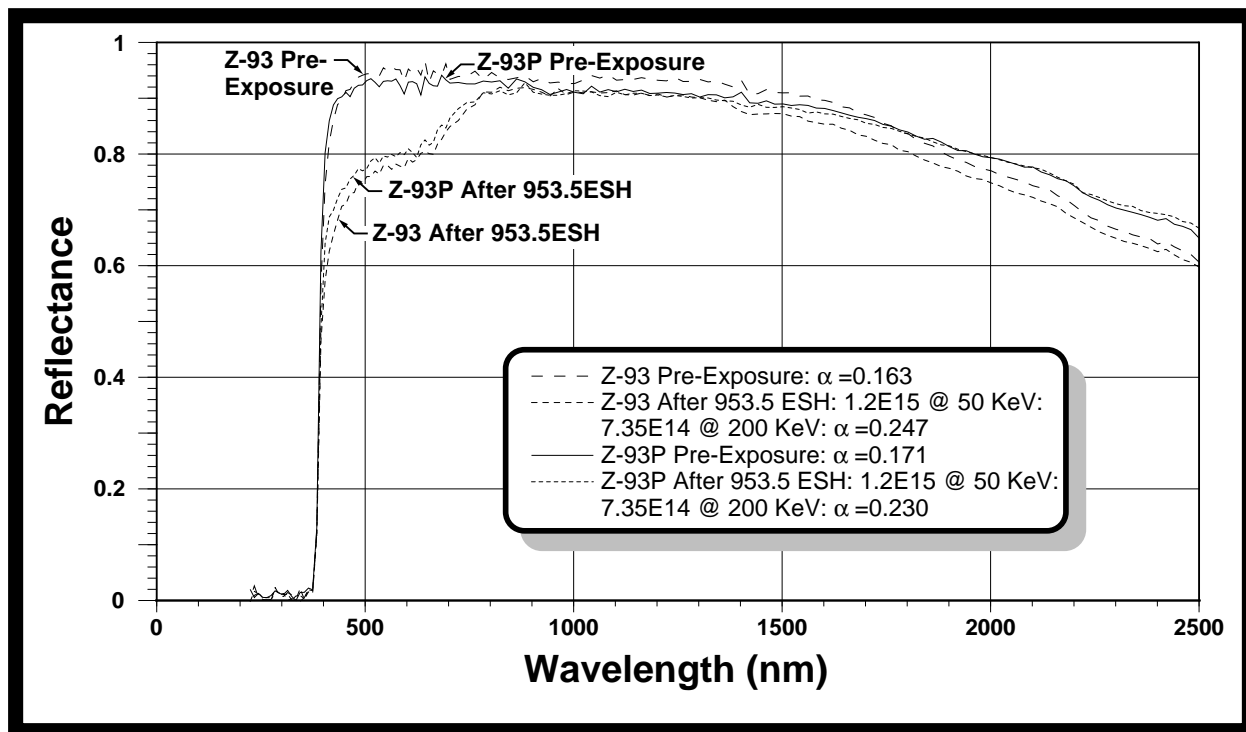
Figure 9. In-vacuo reflectance spectra of Z-93 and Z-93P after a cumulative dose of 953.5 ESH of NUV and VUV, 50-KeV electrons at a fluence of 1.2×10^{14} electrons/cm^2 and 200-KeV electrons at a fluence of 7.35×10^{14} electrons/cm^2.

REFLECTANCE RECOVERY INVESTIGATION

Previous data, shown in figure 5, indicate that a reflectance recovery process will occur when Z-93 type paints are damaged with space environmental effects then repressurized with air. The term "bleaching" in this report will refer to those optical property recovery processes induced after introduction of gasses. A bleaching effect is a type of recovery process generally associated with exposure to air or some other gas containing oxygen. Figure 5 shows a bleaching effect after the Z-93 sample was irradiated and then repressurized with air as a fill gas. Throughout this report, the term recovery process refers to those processes that produce an increase in the reflectance of a material after the material experienced a decrease in reflectance due to an environmental exposure.

Figure 7 shows a recovery process that occurred in the IR portion of the Z-93 spectrum. This sample experienced reflectance recovery while exposed to NUV, VUV, 50-KeV electrons, and high vacuum of 5×10^{-8} torr. This process could be activated by NUV or VUV exposure, continued exposure to 50-KeV electrons, or could be simply time activated. These data indicate the existence of a recovery process activated by an effect other than bleaching. An effort was initiated to determine (1) if the samples experience any recovery if exposure to NUV and VUV continues, and (2) can pure nitrogen be used as a back-fill gas to eliminate or reduce the bleaching effect that was observed when back-filled with air. To determine if any recovery will occur if the samples are further exposed to NUV and VUV, the Z-93 and Z-93P samples were exposed to an additional 190 ESH of NUV and VUV. Figure 10 shows a small recovery in the IR part of the spectrum and increased degradation in the visible part of the spectrum. After the additional 190 ESH, the samples remained in a dark vacuum, all photon sources were removed, and samples were in a vacuum of 5×10^{-8} torr, for 56 hours. Figure 11 shows no substantial recovery occurred after the 56 hours of dark vacuum exposure. This indicates that long times in vacuum are not a prime factor in the recovery process.
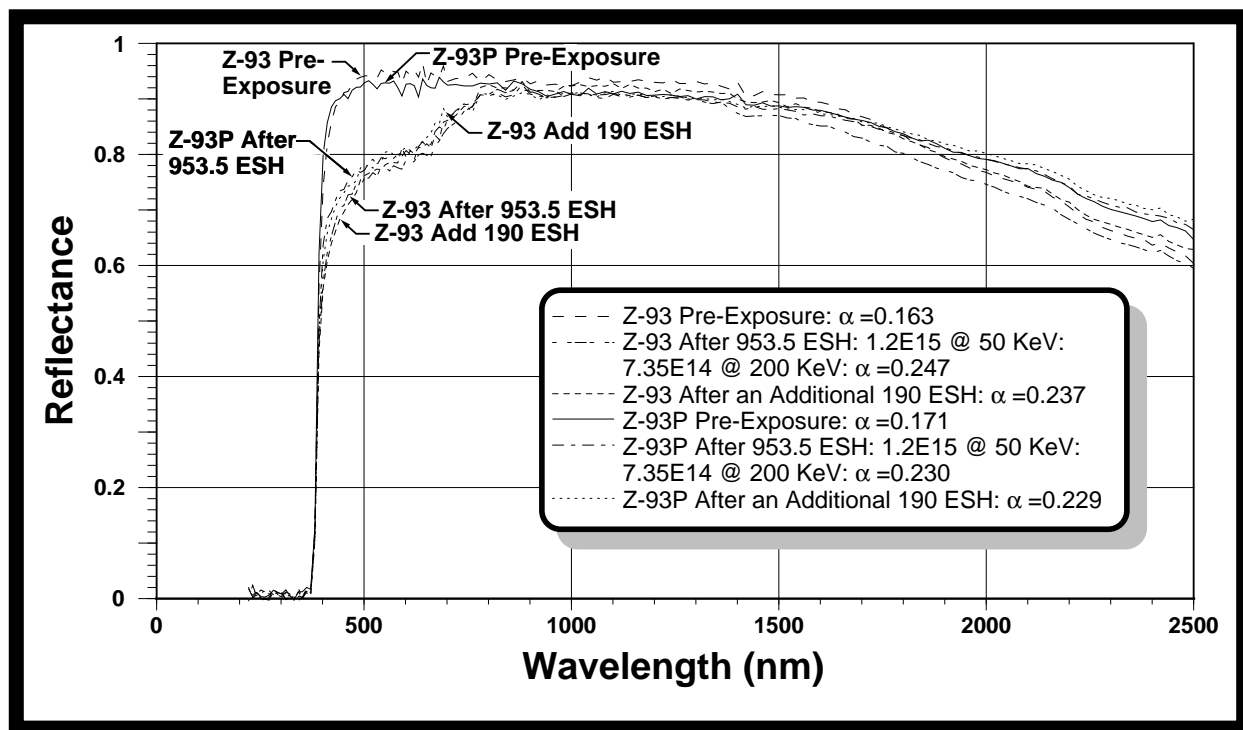
Figure 10. In-vacuo reflectance spectra of Z-93 and Z-93P showing the effects of an additional exposure of 190 ESH of NUV and VUV. These data show no substantial recovery due to the additional NUV and VUV exposure.
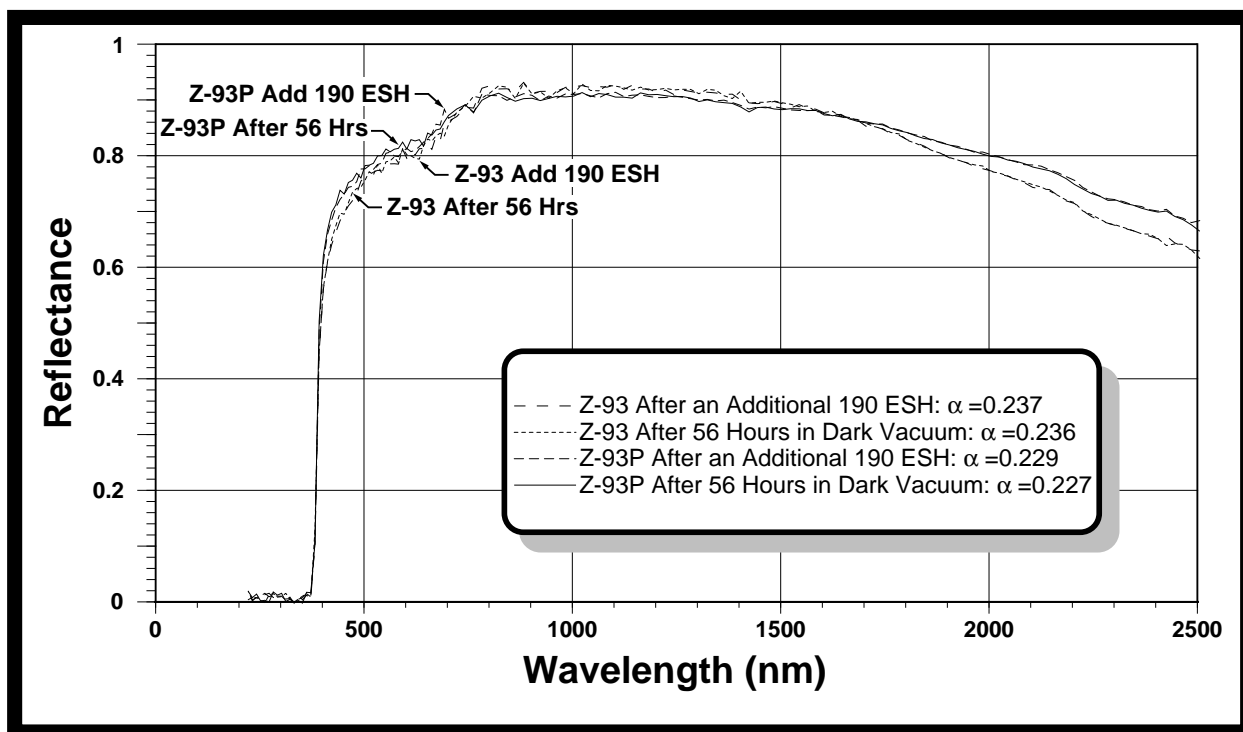

Figure 11. In-vacuo reflectance spectra of Z-93 and Z-93P after 56 hours in dark vacuum.

An attempt was made to back-fill the CEE test chamber with nitrogen, from liquid nitrogen boil-off, at a rate sufficient to monitor reflectance changes as a function of pressure. The nitrogen leak valve utilized lacked the required sensitivity for this procedure to be implemented, so the reflectance was measured as a function of time. The in-vacuo reflectance system was configured to monitor the sample reflectance at 600 nm. The sample analyzed was Z-93P. Figure 12 shows that over a 10-minute nitrogen back-fill time, the reflectance at 600-nm wavelength recovered by approximately 47 percent. After 10 minutes of nitrogen back-fill, the test chamber reached atmospheric pressure. A reflectance curve of the Z-93 and Z-93P samples after 1 hour in a closed nitrogen environment was generated, and these data are shown in figure 13. The samples remained in a closed nitrogen environment for a total of 113 hours, with an interim measurement taken after 41 hours to determine if nitrogen produced any bleaching effects on the samples. Results from this test indicate that extended exposure to a closed nitrogen environment produces little change in reflectance beyond the first 10 minutes of nitrogen exposure. These data are shown in figure 14.

After the reflectance spectra was obtained for the Z-93 and Z-93P samples, which remained in a closed nitrogen environment for 113 hours, the samples were removed from the CEE test system and measured, in air, by the laboratory portable spectroreflectometer (LPSR). The transit time, in air, between the closed nitrogen environment of the CEE test chamber and the LPSR measurement was approximately 15 minutes. The results of this 15-minute exposure to air are shown in figure 15. After this measurement in air, the samples were placed in a standard sample holder and kept in a dark environment for 510 hours. Figure 15 shows that the samples experienced a slight recovery during the 510 hours in the dark ambient environment.
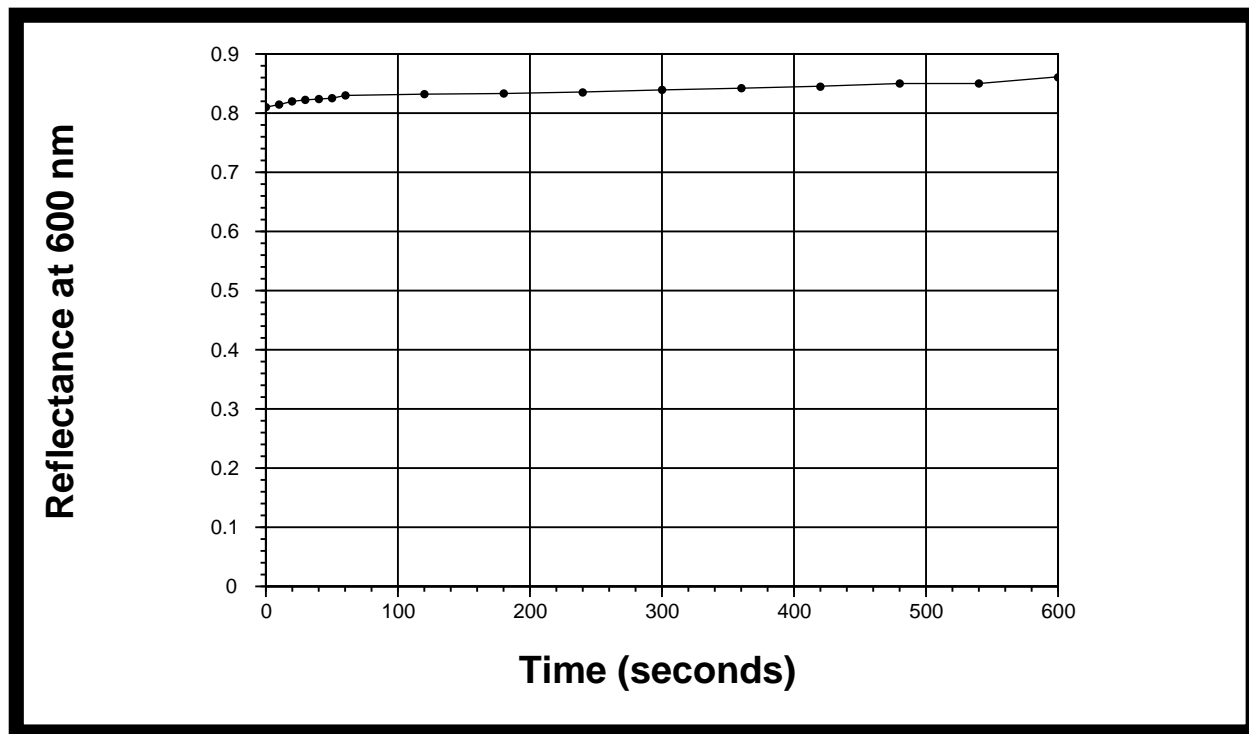

Figure 12. Data showing the percent reflectance recovery at 600 nm of the Z-93P sample during repressurization with nitrogen.
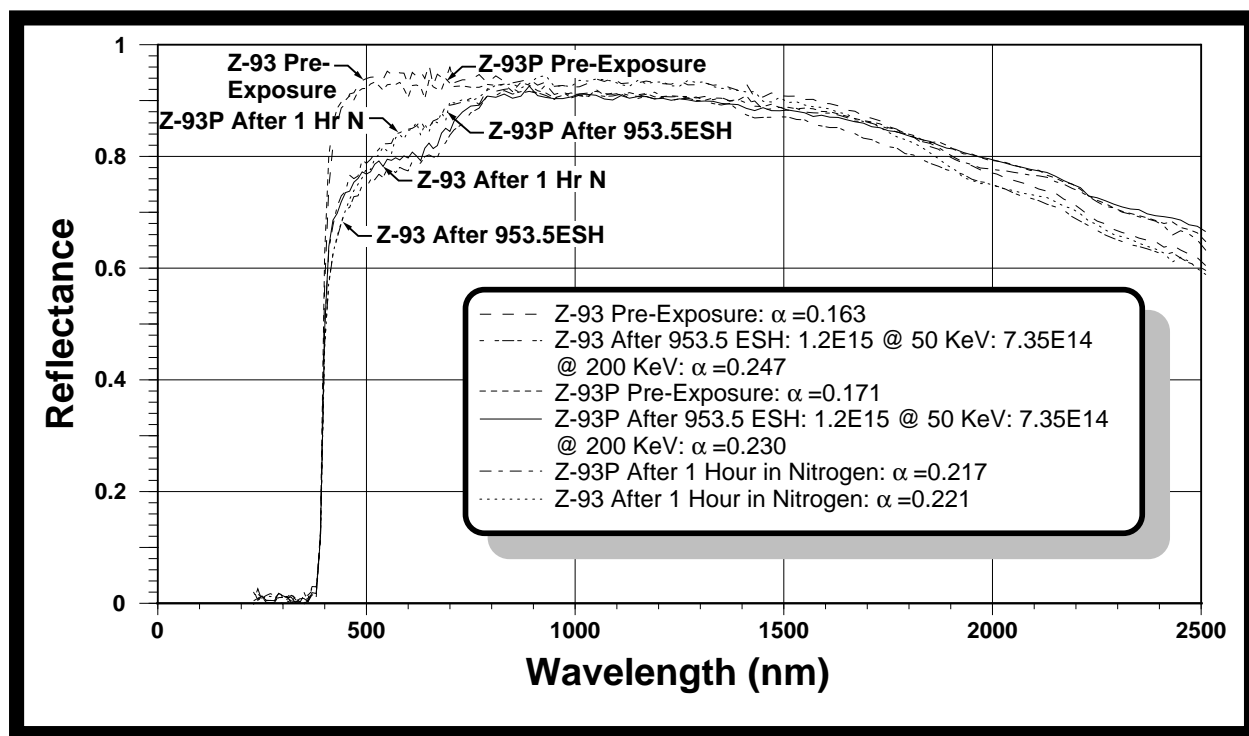
Figure 13. Reflectance spectra of Z-93 and Z-93P after 1 hour in a dark closed nitrogen environment.
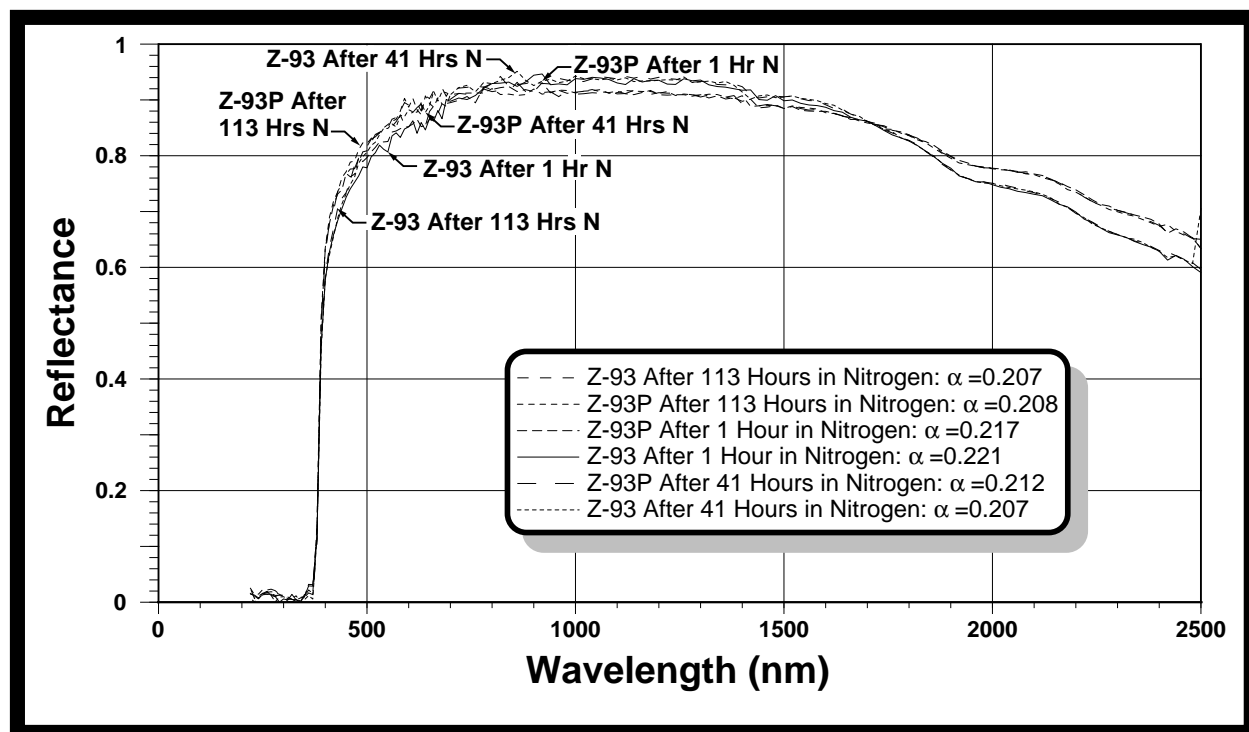

Figure 14. Reflectance of Z-93 and Z-93P after 1 hour, 41 hours, and 113 hours in a dark closed nitrogen environment.
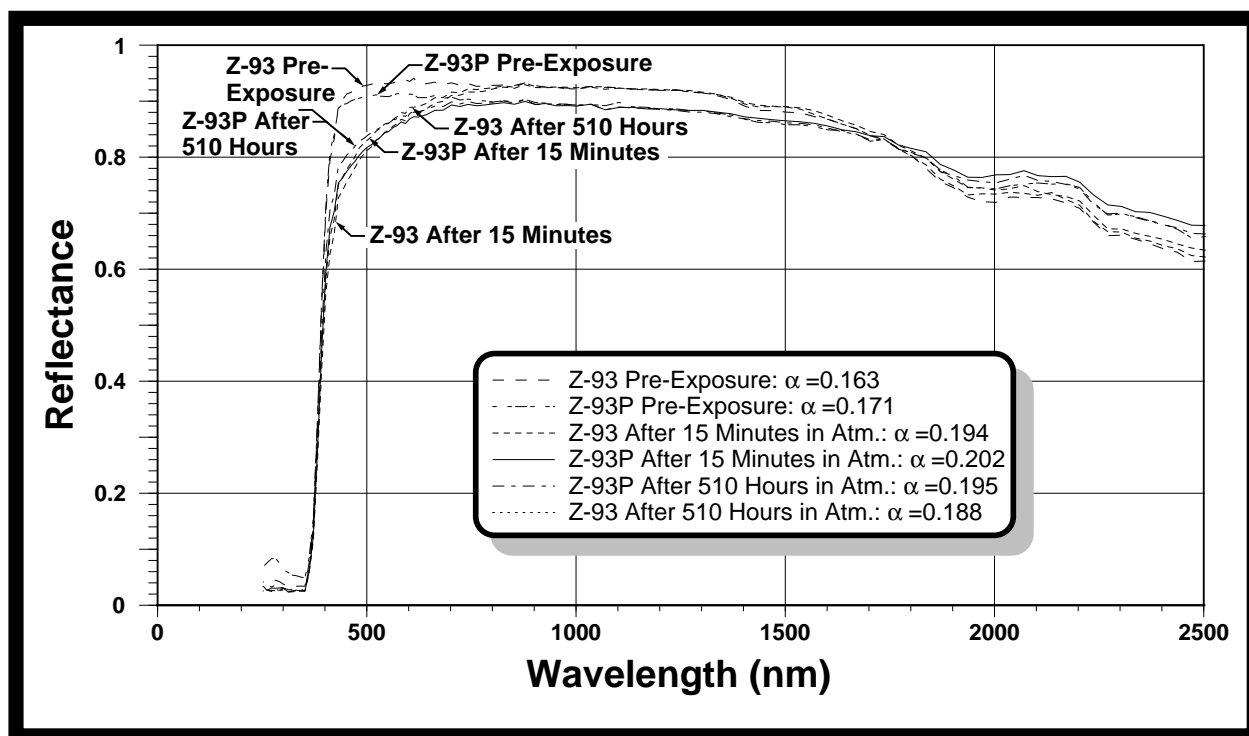
Figure 15. Reflectance spectra of Z-93 and Z-93P after 15 minutes and 510 hours in ambient environment.

CONCLUSIONS

The IIRTI manufactured samples of Z-93 and Z-93P were exposed to equivalent doses, not considering the unknown proton exposure, of NUV, VUV, 50 KeV, and 200 KeV electrons. This test shows similar degradation in both samples when subjected to equivalent space environmental effects exposure. A conclusion of this comparative analysis test is that Z-93P is a suitable replacement for Z-93.

During the course of this test, many other observations were made concerning Z-93 response to a simulated space environment. The optical properties of Z-93 were observed to recover while irradiated in vacuum, as shown in figure 7, between the wavelengths of 800 and 2,500 nm. The mechanism that activates this recovery is being investigated. Variables that possibly influence this recovery are time, residual gases in the vacuum, sample surface contamination, energy deposition in the sample, and possibly temperature. Energy deposition could be from the NUV, VUV, or 50 KeV electrons or any combination of these sources. A theory to explain the broad-band absorption and subsequent recovery from 800 to 2,500 nm pertains to valence band electron excitation.[6] At the present time it is not known if the valence band excitation occurs in the ZnO pigment or the potassium silicate binder. The recovery process is theorized to be the de-excitation or the decay of excited conduction band electrons back to the valence band. More work is needed to understand and document this recovery phenomena.

The nitrogen back-fill test was performed to determine if the bleaching effects, commonly observed when back-filled with air, could be eliminated or reduced and thus provide a guideline to measure sample reflectance ex-vacuo with some credibility. The results of this test show that Z-93 samples experience a recovery in solar alpha of approximately 52 percent when back-filled and maintained in a closed nitrogen environment for 113 hours. It should be noted that this 52-percent recovery of solar alpha was observed after a specific CEE exposure was applied to the Z-93 sample. This specific dose was 953.5 ESH of NUV and VUV, 1.2×10^{15} electrons/cm^2 at 50 KeV, and 7.35×10^{14} electrons/cm^2 at 200 KeV. Another Z-93

sample was exposed to a CEE of 1156.5 ESH of NUV and 3.53×10^{15} electrons/cm^2 at 50 KeV then repressurized with air. The solar alpha of this sample recovered by 71 percent after 15 minutes in air, as shown in figures 5 and 16. Figure 17 summarizes the change of Z-93 and Z-93P solar alpha during this test. Solar alpha of both Z-93 and Z-93P increased with increasing CEE and solar alpha recovered as the samples were exposed to nitrogen and later, air. These results indicate that nitrogen repressurization can decrease the rate of reflectance recovery and, therefore, has a potential use in obtaining credible reflectance measurements ex-vacuo. The authors emphasize that this specific use of nitrogen, as a repressurant, requires further development.
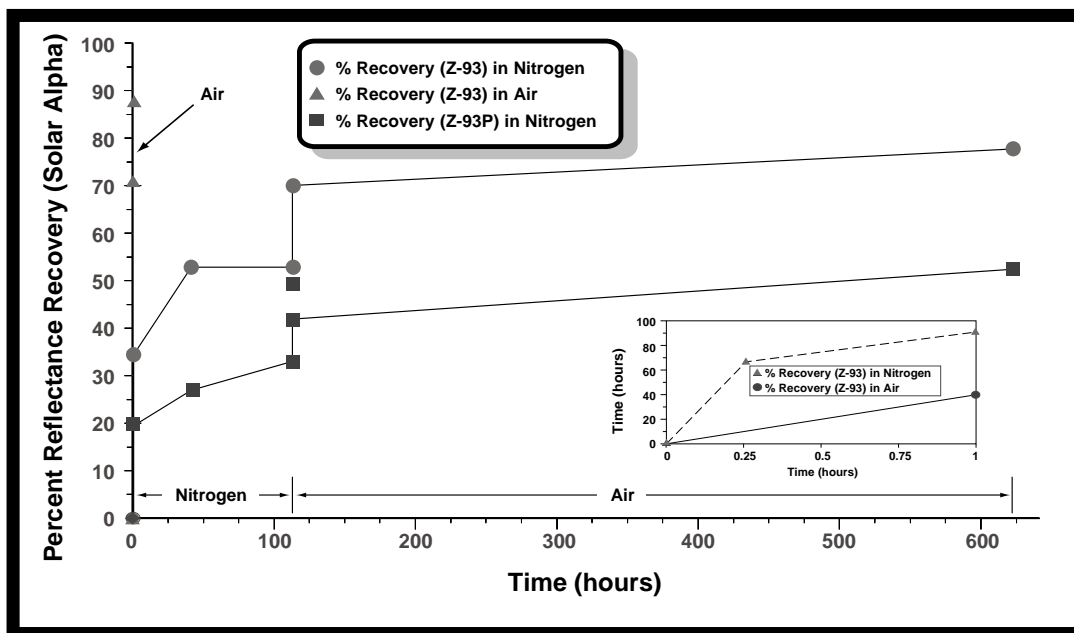

Figure 16. Percent reflectance recovery of Z-93 solar alpha and Z-93P solar alpha with time. This graph shows that the rate of reflectance recovery of the Z-93 solar alpha was less when nitrogen was used as a repressurizing gas.
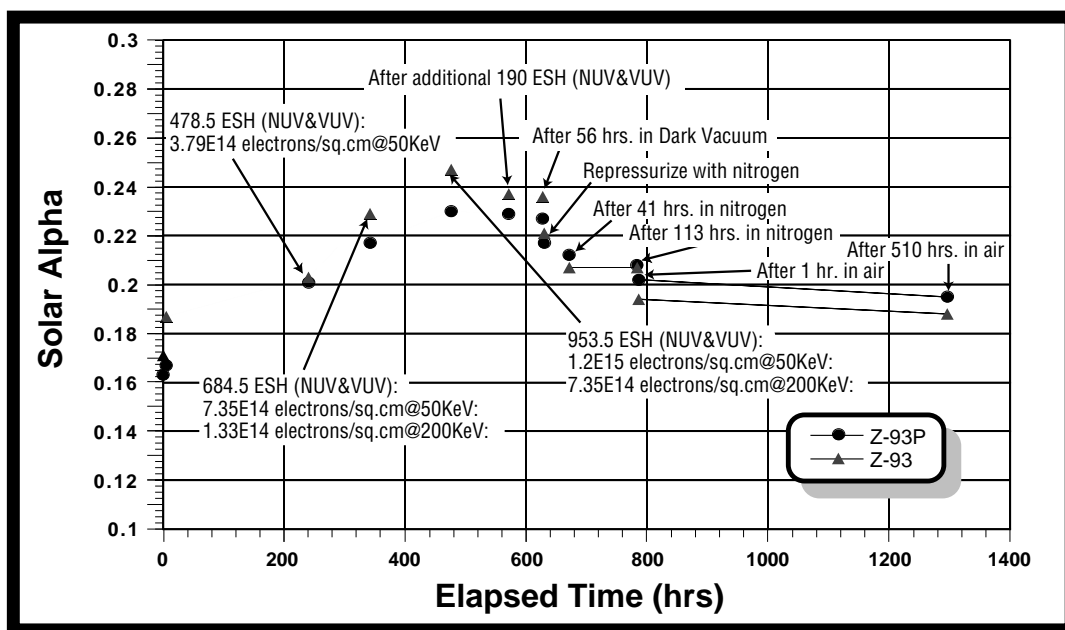

Figure 17. Summary of Z-93 and Z-93P solar alpha change during the CEE test.

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